

The 3rd AAPG/SEG/EAGE International Geosciences Student Conference

29-31 May 2012, Belgrade, Serbia

PROCEEDINGS

The 3rd AAPG/SEG/EAGE International Geosciences Student Conference

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Publisher: Association of Geophysicists and Environmentalists of Serbia (AGES)

For Publisher: Snežana Komatina-Petrović, Association of Geophysicists and Environmentalists of Serbia (AGES)

Printed by: PROOF, Belgrade

Copies: 500

ISBN

All papers in the Proceedings are reviewed

The Proceedings are published with the financial support of the Ministry of Science and Education of Serbia

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CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

55(082)
624.13(082)
620.91:550.36(082)
502/504(082)

AAPG/SEG/EAGE International Geosciences
Student Conference (3 ; 2012 ; Beograd)
[Proceedings] / The 3rd AAPG/SEG/EAGE
International Geosciences Student Conference,
29-31 May 2012, Belgrade, Serbia ; [organizer
Association of Geophysicists and
Environmentalists of Serbia (AGES) ; editor
Saša Smiljanić]. - Belgrade : #Association of
Geophysicists and Environmentalists of Serbia
(#AGES), 2012 (Belgrade : Proof). - [248]
str. : ilustr. ; 30 cm

Tiraž 500. - Bibliografija uz pojedine
radove.

ISBN 978-86-913953-5-3
1. Association of Geophysicists and
Environmentalists of Serbia (Beograd)
a) Геологија - Зборници b) Инжењерска
геологија - Зборници c) Геотермална
енергија - Зборници d) Животна средина -
Заштита - Зборници
COBISS.SR-ID 191120908

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Arsenic occurrence in groundwater of Southern part of Pannonian basin (Serbia)

Marina Cuk*, Maja Todorovic, Jovana Milosavljevic

Summary

Groundwater for water supply of the population on the territory of Vojvodina shows unsatisfactory chemism, which is the consequence of the complexity of geological and hydrochemical characteristics of the geoenvironment. The increased alkalinity of this water, the high content of natural organic matters and the high concentration of arsenic and iron are general features of this water. The concentration of arsenic in the groundwater frequently and manifold exceeds the allowed value (prescribed 10 $\mu\text{g/L}$) in drinking water. On the basis of more than 400 analyses of groundwater, a prognostic hydrochemical map of groundwater has been completed from the aspect of the arsenic area. As the most endangered districts, there are singled out: Northern Bačka and Middle Banat. The most critical situation is in Subotica, Zrenjanin and Kikinda, with arsenic concentrations in drinking water reaching values over 200 $\mu\text{g/L}$. The district of Srem is singled out by qualitative groundwater and there, arsenic concentrations are within allowed values in drinking water.

Introduction

Vojvodina is a northern province of the Republic of Serbia and covers the surface of 21 506 km². It embraces southern parts of the Pannonian Basin (Figure 1) whose natural border in Serbia is represented by the Danube River (almost as far as the Tisa River mouth) and a geomorphological water divide following the Fruška Gora ridge. The western border with Croatia is also represented by the Danube River while to the northern and northern –eastern side Vojvodina is bordered by the state border to Hungary and Rumania. The overall population of Vojvodina is about two million.



Fig. 1 – Geographical position of study area

A large number of people in Vojvodina, and in other countries occupying the area of the Pannonian Basin as well, face the problem of water supply owing to increased arsenic concentrations in groundwater. In Croatia, Osijek-Baranja and Vukovar-Srijem are emphasized as endangered areas with arsenic concentrations of 491 $\mu\text{g/L}$ in water for water supply, and the age of tapped layers is of Middle and Upper Pleistocene (M. Ujević, Ž. Duić et al. 2010). In the area of Rumanian and Hungarian part of the Pannonian Basin about 500 000 people use groundwater with arsenic concentration above MPC, and arsenic concentrations in groundwater for water supply reach even 240 $\mu\text{g/L}$ (Helen A.L. Rowland, Enoma O. Omoregie, 2010.).

The increased content of As in drinking water can be considered a global problem. In Taiwan, Argentina and Chile, concentrations of this element are over 500 $\mu\text{g/L}$. "A black foot disease" was discovered in Taiwan causing periphery vascular disorders with gangrene and skin changes (hyperkeratosis and hyperchromatosis). This disease can be caused by using of water with As concentrations from 0.3 to 0.6 $\mu\text{g/L}$ for a long period. A large number of harmful effects of arsenic on human health

has been identified, such as changes on skin, effects on cardio-vascular and respiratory systems, neurological effects, cancer of skin and other organs (Petruševski B. et.al, 2005).

Owing to high toxicity of arsenic and its wide distribution in a large number of compounds the need for effective monitoring and measuring of arsenic concentration in soil, air and water in surface water and groundwater has arisen (Marković D. et al.2008). The problem of arsenic removing from shallow aquifers is present worldwide, especially after EPA, WHO and other international standards have reduced arsenic MPC in drinking water from 50 to 10 $\mu\text{g/L}$. The standard has been adopted according to which nowadays every tenthousandth man is allowed to fall ill with cancer caused by arsenic with corresponding As content in water of 0.5 $\mu\text{g/L}$ (D. Stojiljković, 2004).

In natural waters, arsenic is present mainly in its inorganic form, which is at the same time more toxic as well. Inorganic arsenic occurs in water in the forms As (V) and As (III). The As (III) compounds are more toxic than the forms made by As (V). Therefore, it is significant to determine the distribution of both As types for qualitative groundwater analyses (Marković D. et al, 2008).

Theory and Methods

The completion of a paper dealing with problems of this kind has required gradualness in collecting and selection of literature in order to approach knowledge gradually and consistently. After getting informed about physico-chemical properties of arsenic, the way of occurrence and distribution in biosphere, then there followed the data collecting of chemical analyses of groundwater for Vojvodina water supply, and afterwards by their processing and interpretation a prognostic hydrochemical map of arsenic regional distribution has been obtained. On the basis of the completed map, a more clear picture of this element distribution in groundwater of Vojvodina is obtained, which indirectly implies the number of inhabitants using water with arsenic concentration over MPC. Chemical analyses of groundwater were processed in the program package for statistics IBM SPSS 19.0. The data were processed statistically and represented graphically by sources and settlements, and as a final result, a prognostic hydrochemical map of arsenic regional distribution in groundwater for Vojvodina water supply was completed (1:650.000), whereby ESRI package ArcGIS 9.3 was used.

As to the quality of groundwater for Vojvodina water supply, it is considered to be of conditionally poor quality, but by technological procedures it can reach drinking water quality regulated by law. Parameters that do not meet regulations are the following: iron, manganese, ammonia ion, and arsenic. Waters are generally of hydro carbonate, sodium to calcium-magnesium types. Water exchange is slackened, thus groundwater is in permanent interaction with sediments. The temperature of groundwater is slightly increased, and pH values are neutral to mildly alkaline. To complete this paper, there have been analysed 22 water systems-433 facilities among which less than 50% meets the criteria for arsenic in drinking water (Table 1, Figure 2).

Table 1. Basic statistical parameters on basis of arsenic concentration data processing at facilities for water supply of Vojvodina

Number of analyses	433
Minimum As [$\mu\text{g/L}$]	0
Maximum As [$\mu\text{g/L}$]	234
Mean Statistic	21.11

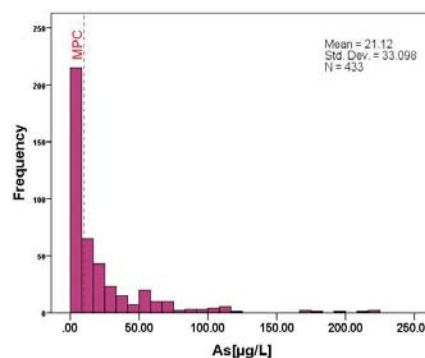


Fig. 2 – Distribution of mean arsenic concentrations in water supply systems in Vojvodina

Some authors consider arsenic in groundwater of Vojvodina a contaminant (Jovanović, D. et al. 2011), and its origin anthropogenic, namely originating from pesticides used in the region of Vojvodina owing to intensive agriculture. Hydrogeologically, the region of Vojvodina is comprised of Neogene and Quaternary deposits of high thickness with numerous water-bearing environments of various structural type of porosity and with clay interlayers not allowing penetration of contaminating matters from the surface of the terrain. Thereby, for the water supply system, wells were drilled at deeper depths (70 - 250 m), in Pliocene-Pleistocene sediments, sands, thick more than ten metres and unlimited spatial development (basic water-bearing complex-BWC) representing a basis of all existing sources. Also, in the first the most shallow aquifer tapped by rural wells (to 10m) there was not recorded increased arsenic concentration (Ujević M. et al, 2010.), thus it is doubtless that arsenic geological origin in groundwater in the region of the Pannonian Basin is in question. Favourable conditions for arsenic migration are poor alkaline pH values of groundwater, reduction environment and the presence of organic matter (Appelo and Postma, 2005).

Examples

On the basis of processed chemical analyses of the groundwater a prognostic hydrochemical map of groundwater was completed from the aspect of arsenic regional distribution (Figure 3). As the most endangered areas, there are singled out Northern Bačka and Middle Banat. Arsenic values in drinking water over 200 µg/L were recorded in some wells for water supply in Subotica, Zrenjanin and Kikinda. In Southern Banat (Vršac, Kovin, Bela Crkva), there is almost no increased arsenic concentration in drinking water. The region of Srem is singled out by qualitative water, and in this region arsenic concentration is within allowed values in drinking water.

The region of Northern Bačka is supplied by water via organised central water supply systems. Smaller rural settlements are supplied by water from their own local sources. The largest town of this region is Subotica (143260 inhabitants) and for the water supply of the town wider area, there are 13 sources in exploitation: Palić, Bački Vinogradi, Bajmok, Čantavir, Đurđin, Mišičevo, Mala Bosna, Kelebija, Novi Žednik, Stari Žednik, Višnjevac, Zmajevo and Kula Horgoš (Mandić, M., Papić P.). Arsenic concentration from the sources for the water supply of Subotica ranges from 2 – 234 µg/L (Table 2).

Table 2. Basic statistic parametrs based on arsenic concentration data processing in facilities for water supply of Subotice

N	13
Minimum	2
Maximum	234
Mean Statistic	110.84

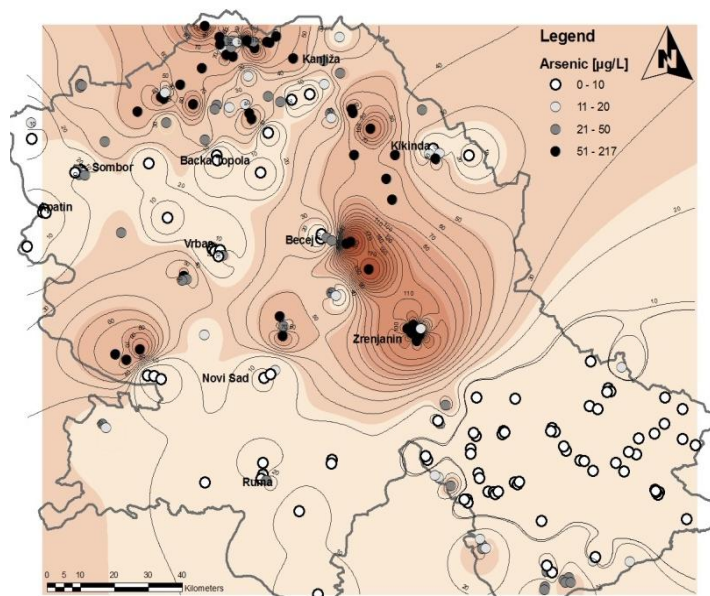


Fig. 2 – Prognostic Hydrochemical map of arsenic in groundwater water for supply systems of Vojvodina

Conclusions

Arsenic is a naturally distributed element in the atmosphere, lithosphere, hydrosphere and biosphere, known as a toxic and cancerous element. It is distributed in the geological environment of the Pannonian Basin, in layers from which groundwater is exploited for water supply. There are about two million inhabitants in the region of Vojvodina and a large percentage of the population is in the position to use drinking water with arsenic concentrations above MPC. The most endangered is the region of Northern Bačka (Subotica), Middle and Northern Banat (Zrenjanin, Bečej and Kikinda), while in the regions of Southern Banat and Srem drinking water is of significantly better qualitative characteristics. Arsenic in groundwater of Vojvodina is of geological origin and in conditions such as a reduction environment, the occurrence of organic matters and mildly alkaline water character improve the migration of arsenic.

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